

Regional variation of organic functional groups in aerosol particles on four U.S. east coast platforms during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign

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[1] Submicron atmospheric aerosol samples were collected during the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) 2004 campaign on four platforms: Chebogue Point (Nova Scotia, Canada), Appledore Island (Maine), the CIRPAS Twin Otter over Ohio, and the NOAA R/V *Ronald H. Brown* in the Gulf of Maine. Saturated aliphatic C-C-H, unsaturated aliphatic C=C-H, aromatic C=C-H, organosulfur C-O-S, carbonyl C=O, and organic hydroxyl C-OH functional groups were measured by calibrated Fourier Transform Infrared (FTIR) spectroscopy at all four sampling platforms. The ratio of molar concentrations of carbonyl C=O to saturated aliphatic C-C-H groups was nearly constant at each sampling platform, with the Twin Otter samples having the lowest ratio at 0.1 and the three more coastal platforms having ratios of 0.4 and 0.5. Organic mass (OM) to organic carbon (OC) ratios follow similar trends for the four platforms, with the Twin Otter having the lowest ratio of 1.4 and the coastal platforms having slightly higher values typically between 1.5 and 1.6. Organosulfur compounds were occasionally observed. Collocated organic aerosol sampling with two Aerodyne aerosol mass spectrometers for OM, a Sunset Laboratory thermo-optical analysis instrument for OC, and an ion chromatography-particle into liquid sampler (IC-PILS) for speciated carboxylic acids provided comparable results for most of the project, tracking the time series of FTIR OM, OC, and carbonyl groups, respectively, and showing simultaneous peaks of similar magnitude during most of the project. The FTIR/IC-PILS comparison suggests that about 9% of the carbonyl groups found in submicron organic particles on the Twin Otter are typically associated with low molecular weight carboxylic acids.

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1. Introduction

[2] Organic matter constitutes an important fraction of aerosol mass, both in remote and urban locations [Turpin

and Lim, 2001]. The presence of organic compounds in aerosol particles is due to primary emissions and secondary organic aerosol (SOA) formation. SOA can be formed by condensation of species produced by gas phase oxidation of volatile compounds. The chemical composition of the organic fraction affects the hygroscopicity of aerosol particles which in turn affects the aerosol size distribution, residence time in the atmosphere and optical properties [Markowicz *et al.*, 2003; Kim *et al.*, 2006].

[3] Although numerous studies have been performed to characterize polar and nonpolar components of organic aerosols, only a small percentage of the organic mass has been resolved by traditional analytical methods [Saxena and Hildemann, 1996; Turpin *et al.*, 2000]. Infrared spectroscopy has been used to investigate the organic functional group composition of atmospheric aerosol particles for more than 30 years [Blanco and McIntyre, 1972; Dangler *et al.*, 1987].

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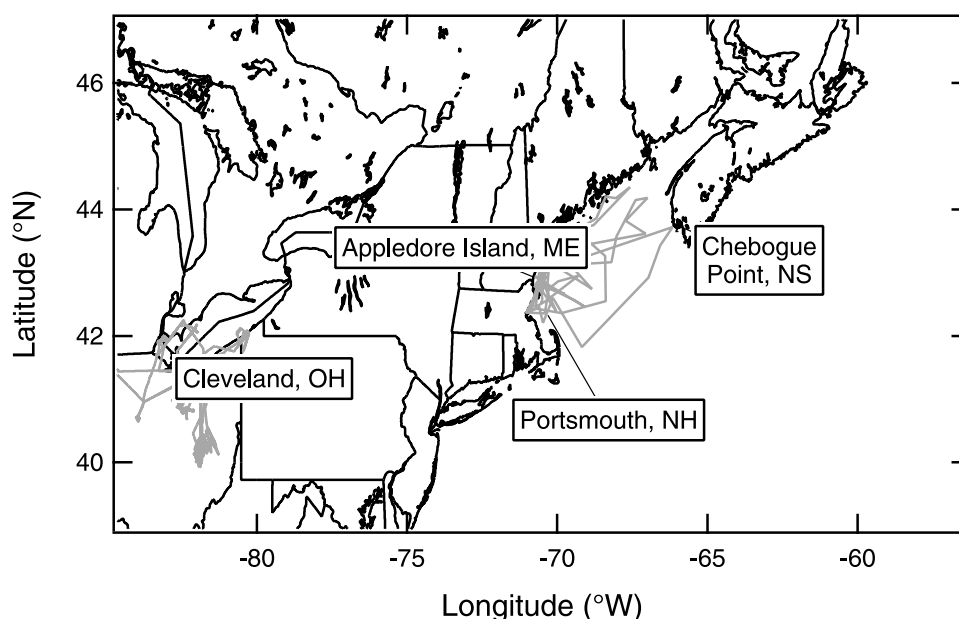


Figure 1. Sampling platform locations, showing the Chebogue Point site (Nova Scotia, Canada), the Appledore Island site (Maine), the R/V *Ronald H. Brown* cruise track (started in Portsmouth, NH), and CIRPAS Twin Otter flight tracks (based in Cleveland, Ohio) in grey.

Recent work has provided a calibrated methodology for quantitative estimates of the functional group composition of organic aerosol [Maria *et al.*, 2002, 2003].

[4] The organic fraction of particles is composed of a large variety of compounds: alkanes, alkenes and aromatic compounds, monocarboxylic and dicarboxylic acids, alcohols and saccharides, organic sulfur compounds (sulfates and sulfonic acids), organic nitrogen compounds (organic nitrates, amines, imines, and amino acids), and polyfunctional oligomers. Some of these organic families are more hydrophobic and others show higher water solubility and uptake. Organic particles that are dominated by saturated and unsaturated carbon chains are less hygroscopic than an aerosol mass characterized by higher concentration of polar groups (hydroxyl and carboxylic acids, for example). The presence of heteroatoms in organic molecules may increase both their polarity and water solubility. Oxygenated functional groups are more common than sulfur and nitrogen in atmospheric particles.

[5] Oxygenated compounds are usually characteristic of SOA [Gao *et al.*, 2004; Lim and Ziemann, 2005] but may be found in primary aerosol particles as well (e.g., dicarboxylic acids have been identified in primary sea salt particles [Mochida *et al.*, 2002]). Carboxylic acids and saccharides have been detected in forest biogenic emissions [Graham *et al.*, 2003]. Ketones are components of plant waxes that contribute to atmospheric particles in rural areas [Simoneit and Mazurek, 1982]. The contribution of oxygenated compounds to total organic mass depends on both the aerosol sources and the chemical and physical processes that affect the atmospheric processing of the aerosol particles.

[6] During the ICARTT experiment in summer 2004, submicron particle samples were collected at four different platforms. Organic functional groups were quantified by Fourier Transform Infrared (FTIR) spectroscopy. This study

compares the similarities and differences in the measured unsaturated aliphatic C=C–H and saturated aliphatic C–C–H groups, oxygenated organic functional groups, organic mass to organic carbon ratios to illustrate the trends in organic composition at each platform, and the systematic differences between the upwind continental particles measured in Ohio and the downwind coastal particles on Chebogue Point, Appledore Island, and the R/V *Ronald H. Brown*. This study also affords the unique opportunity for a comprehensive intercomparison of four independent methods of quantifying organic composition.

2. Measurements

[7] Submicron aerosol samples have been collected in summer 2004, during the ICARTT experiment, at two ground stations (Chebogue Point, Nova Scotia, Canada, and Appledore Island, Maine) and on two mobile platforms (the CIRPAS Twin Otter and the NOAA R/V *Ronald H. Brown*) [Fehsenfeld *et al.*, 2006]. Measurements at Chebogue Point and Appledore Island included a suite of online gas and particle chemical and physical measurements [Williams *et al.*, 2007; Russell *et al.*, 2007; Fischer *et al.*, 2006]. The CIRPAS Twin Otter performed a total of 12 flights, investigating Ohio power plant emissions and regional aerosol background properties [Sorooshian *et al.*, 2006]. The R/V *Ronald H. Brown* collected particle samples in the Gulf of Maine, sampling urban plumes from Boston and New York, as well as aged industrial plumes from Midwestern regions [Quinn *et al.*, 2006]. Ground platform locations and flight and cruise tracks are illustrated in Figure 1.

[8] Aerosol particles were sampled on 37 mm Teflon filters for between 30 min and 24 hours, depending on aerosol loading. Samples collected during the Twin Otter flights are generally characterized by a shorter collection

Table 1. FTIR Absorption Characteristics for Organic Functional Groups

Functional Group	Absorption Frequencies, cm^{-1}	Quantified Peak, cm^{-1}	Absorptivity, abs^{-1}a	Detection Limit, μmol of Bond
Saturated aliphatic C-C-H	1450, 2800–3000	2850–2920	0.895	0.013
Unsaturated aliphatic C=C-H	2900–3100	2980	3.8	0.122
Aromatic C=C-H	3000–3100	3050	8.7	0.035
Carbonyl C=O	1640–1850	1720	0.062	0.009
Organic hydroxyl C-OH	3100–3500	3350	0.057	0.006
Organosulfur C-O-S	876	876	0.031	0.002
Amines C-NH	3400, 1630	–	–	–

^a Absorptivity is the micromole of functional group per unit of peak area (in absorbance). The calibration of absorptivity may be instrument-specific with values that differ slightly on the basis of the detector used [cf. *Maria et al.*, 2003].

interval in order to collect two or more samples during the 4 to 6 hour flights. Teflon filters were stored in polystyrene petri dishes, sealed with Teflon tape and kept at approximately -4°C for later analysis. Identification and quantification of organic and inorganic functional groups were carried out by transmission FTIR spectroscopy. During the ICARTT 2004 campaign more than 250 samples and an equal number of field blanks were collected and analyzed on the four platforms. None of the blanks showed detectable quantities of organic functional groups.

2.1. FTIR Spectroscopy

[9] FTIR analyses were completed with a Bruker Tensor 27 FTIR Spectrometer with a DTGS detector. FTIR spectra were measured in transmission mode in the range between 400 and 4000 cm^{-1} , with a spectral resolution of 4 cm^{-1} and 32 scans for each spectrum. Blank filters were scanned before sampling and aerosol spectra were obtained by subtraction of the blank spectra from the corresponding sample spectra. Ambient aerosol spectra are usually characterized by broad double peaks in the absorption from 2800 to 3400 cm^{-1} for ammonium. This interference was corrected by subtracting a reference spectrum of ammonium sulfate, normalized to the ammonium peak at 3200 cm^{-1} . Table 1 lists the functional groups identified during the ICARTT experiment and the location of the associated peak in absorbance. Here the terms “saturated aliphatic C-C-H groups” and “unsaturated aliphatic C=C-H groups” indicate C-H bonds typical of alkane and alkene molecules, respectively. “Aromatic C=C-H groups” refer to C-H bonds from a benzenic ring structure. The identification of functional groups used multiple absorption peaks, while the quantification was based on an absorption peak with negligible interference. 1-docosanol, anthracene, sodium benzoate, 1-docosene, sodium ethyl-sulfate, citric acid and adipic acid have been employed as calibration standards [*Maria et al.*, 2002, 2003]. The absorbance for the detected species varies linearly with the number of moles of bonds and is independent of mixture composition [*Maria et al.*, 2002, 2003]. The error associated with the calibration of a single reference compound is typically 10% of the measured concentration for most functional groups, with the exception of organic hydroxyl C-OH groups for which interference from water, ammonia, and amines increases the error to 22%. The combined uncertainty of reference compounds, peak integration, and absorption artifacts is between 5% and 22% [*Russell*, 2003].

[10] Organic sulfur compounds have been identified in aerosol particles by an absorption peak at 876 cm^{-1} [*Maria*

et al., 2003; *Blando et al.*, 1998]. Carbonate and hydrogen sulfate ions also absorb in the region between 850 and 890 cm^{-1} (http://www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi). Reference samples of carbonates, hydrogen sulfate, and sodium ethylsulfate were prepared using an atomizer (TSI Inc., model 3076) to collect deposits on Teflon filters, which were rinsed with hexane and acetone to separate the organic sulfur compounds by dissolving in organic solvents without removing the less soluble carbonate and hydrogen sulfate ions [*Maria et al.*, 2002]. This sequential rinsing with hexane and acetone was used for those samples with an absorption peak located in the region 850 cm^{-1} – 890 cm^{-1} to distinguish organosulfur compounds from carbonate and hydrogen sulfate ions.

[11] Amines are characterized by two absorption peaks located at 3400 cm^{-1} and 1630 cm^{-1} . Amines were present below detectable amounts for all samples collected at Chebogue Point, on the Twin Otter, and on the R/V *Ronald H. Brown*. Significant amine absorption signals were observed in a few samples collected at Appledore Island. Identification of amines is noted in Figure 2, although their quantification was not possible during this project [*Maria et al.*, 2003].

[12] To convert calculated molar concentration to the mass concentration of equivalent organic carbon (OC), we assume that saturated carbon chains are present mainly as CH_2 groups [*Maria et al.*, 2002]. The concentration of saturated carbon was obtained by multiplying the saturated aliphatic C-C-H bond molar concentration by 6 (corresponding to carbon molecular mass divided by 2 C-H bonds per CH_2 unit). Contributions to organic carbon from unsaturated aliphatic C=C-H, aromatic C=C-H, and carbonyl C=O groups were calculated by multiplying the C=C-H and C=O molar concentrations by 12. To calculate organic mass (OM), the OC concentrations have been scaled to include the mass of associated hydrogen, sulfur, and oxygen atoms [*Maria et al.*, 2002]. Organic mass (OM) is the sum of both OC and associated heteroatoms in carbonyl C=O groups, saturated and unsaturated aliphatic C-H groups, aromatic C=C-H groups, organic hydroxyl C-OH groups, and sulfur from organosulfur C-O-S groups. OM values reported here neglect the contribution of organic nitrogen functional groups.

2.2. Air Mass Categorization

[13] Air masses sampled at Chebogue Point were categorized using the retrorplume summaries calculated by FLEXPART (<http://www.esrl.noaa.gov/csd/metproducts/icartt2004/>). The FLEXPART model is run using two

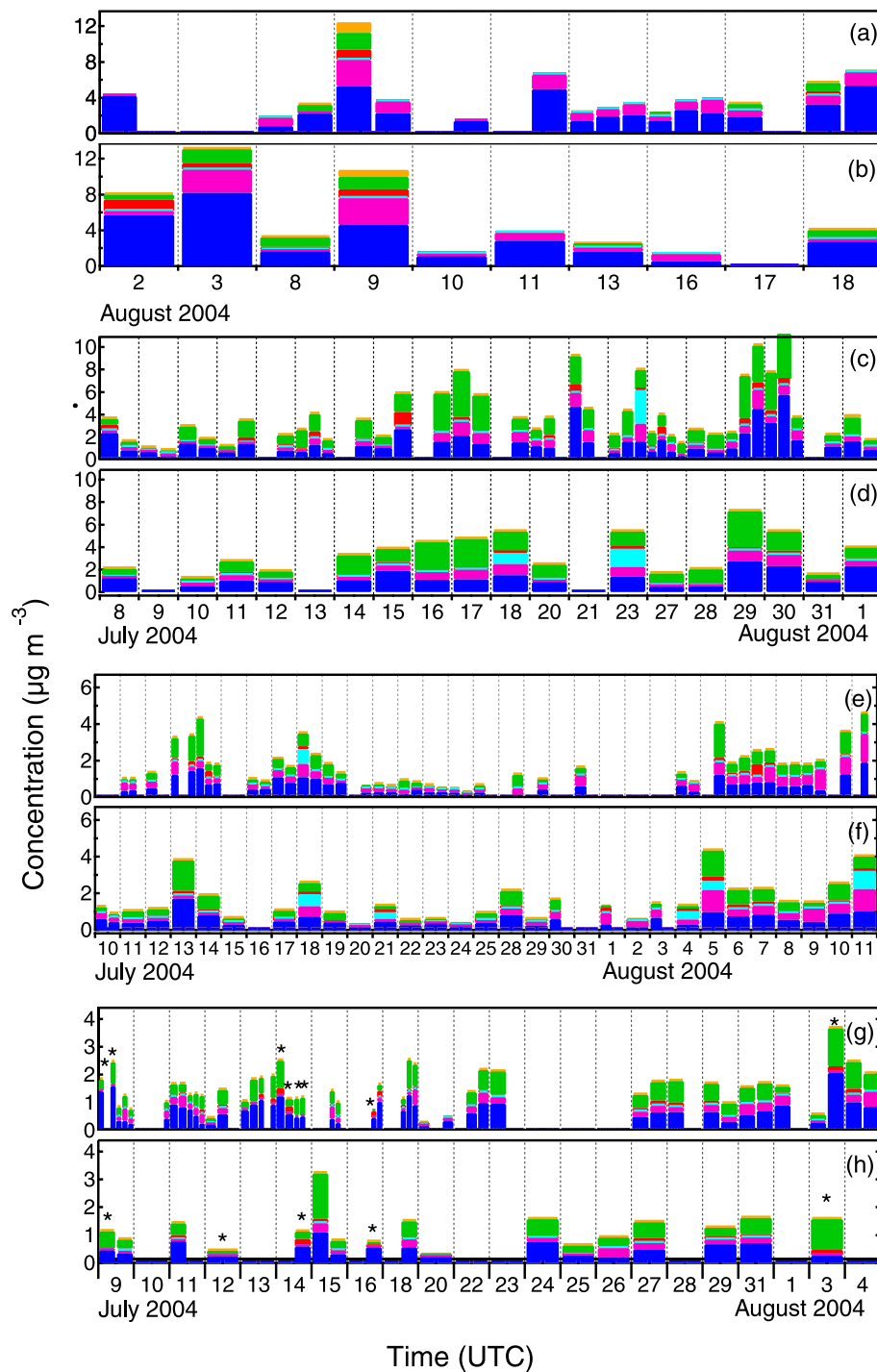


Figure 2. Temporal trends of the measured functional group composition: (a and b) Twin Otter, (c and d) R/V *Ronald H. Brown*, (e and f) Chebogue Point, and (g and h) Appledore Island. For each platform, the lower plot (Figures 2b, 2d, 2f, and 2h) corresponds to functional group composition of cumulative samples (12 or 24 hour collection time), and the upper plot (Figures 2a, 2c, 2e, and 2g) reports simultaneous shorter time samples (3, 4, 6 or 8 hour collection time). All panels show saturated aliphatic C-C-H groups (blue), organic hydroxyl C-OH groups from alcohol and carboxylic acids (pink), aromatic C=C-H groups (light blue), unsaturated aliphatic C=C-H groups (red), carbonyl C=O groups (green), and organosulfur C-O-S groups (yellow) mass concentration. Samples marked by asterisks contained amine C-NH groups.

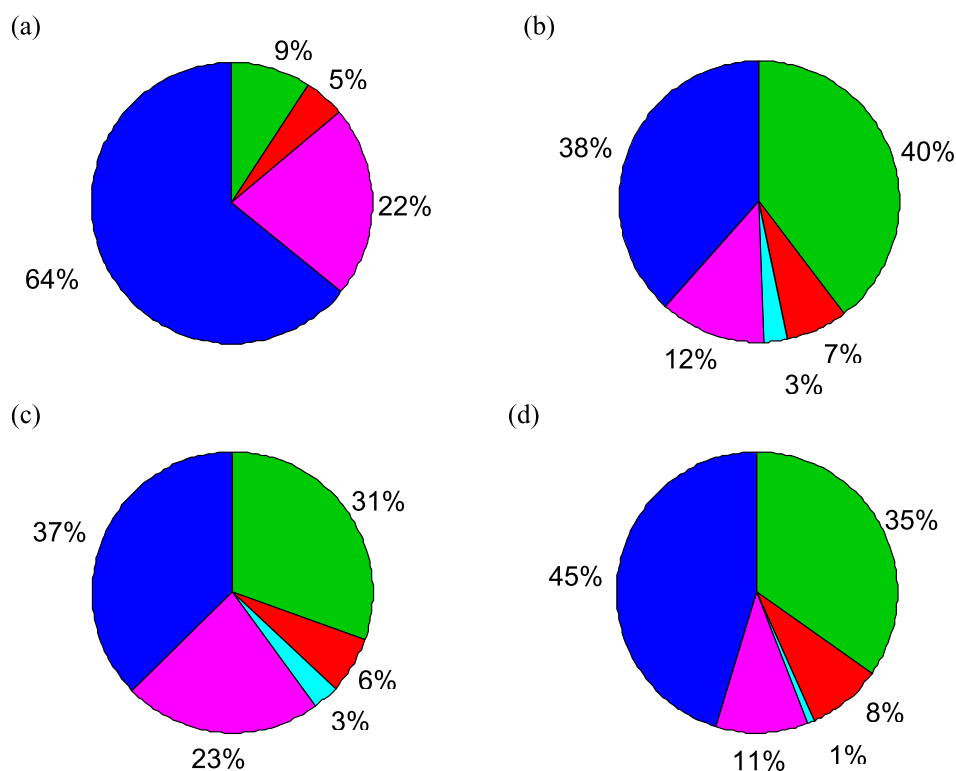


Figure 3. Project average composition of organic mass for (a) Twin Otter, (b) R/V *Ronald H. Brown*, (c) Chebogue Point, and (d) Appledore Island. The color assignments for the organic functional group mass fractions are the same as in Figure 2.

meteorological input data (Global Forecast System model and ECMWF model) with a global resolution of $1 \times 1^\circ$ and a regional resolution of $0.36 \times 0.36^\circ$. FLEXPART is a particle dispersion model that uses the Frost and McKeene inventory for North America with a spatial resolution of 4 km. Air masses sampled at Chebogue Point and Appledore Island were categorized as “U.S.” or “Canada” on the basis of visual inspection of retroplume calculations of the most important emission sources. We considered retroplume trajectories over the 5 days before reaching the sampling platform and their evolution during the sampling interval, including 4 backward simulations during each 12 hour sample. If all simulations for a sampling interval showed the same source locations, the sample was assigned to one of the two source categories. Air mass categorizations for the R/V *Ronald H. Brown* showed that most of those samples were dominated by U.S. influenced air masses [Quinn *et al.*, 2006], whereas the coastal platforms sampled several days that could be characterized by two distinct types of air masses, those dominated by U.S. emissions and those dominated by Canada emissions.

3. Results and Discussion

[14] Saturated aliphatic C-C-H groups, unsaturated aliphatic C=C-H groups, organic hydroxyl C-OH groups from alcohols and carboxylic acids, carbonyl C=O groups from carbonyl in ketones, aldehydes, and carboxylic acids, organosulfur C-O-S groups, ammonium, sulfate, and nitrate were detected during most of the ICARTT 2004 study on all sampling platforms. Figure 2 shows the temporal trend of OM

concentration. The average OM concentrations at Chebogue Point and Appledore Island were 1.7 and $1.4 \mu\text{g m}^{-3}$, respectively. Higher OM concentrations were observed during the R/V *Ronald H. Brown* cruise ($3.6 \mu\text{g m}^{-3}$) and during the CIRPAS Twin Otter flights ($4.6 \mu\text{g m}^{-3}$). The maximum OM concentration measured on board the Twin Otter was $13 \mu\text{g m}^{-3}$. This high OM concentration is probably a result of the proximity to large emission sources, such as coal burning power plants in Ohio [Sorooshian *et al.*, 2006].

[15] OM was dominated by saturated aliphatic C-C-H groups (as shown in Figure 3). The Chebogue Point and Appledore Island platforms show average saturated aliphatic C-C-H concentration of $0.6 \mu\text{g m}^{-3}$. R/V *Ronald H. Brown* and Twin Otter saturated aliphatic C-C-H concentrations were 1.4 and $2.9 \mu\text{g m}^{-3}$, respectively. The average carbonyl C=O group concentration ranged between 0.4 and $0.5 \mu\text{g m}^{-3}$ on Chebogue Point, Appledore Island, and the Twin Otter and reached as high as $1.4 \mu\text{g m}^{-3}$ for R/V *Ronald H. Brown*.

[16] Comparison of the time series of functional groups on the four sampling platforms in Figure 2 shows events that appear to be correlated at two or more different sampling platforms. At Chebogue Point from 12 July (during the biomass burning event reported by Duck *et al.* [2007]), the contribution of carbonyl C=O groups to organic mass started rising. Similar trends in oxygenated functional group composition occurred with a delay of about 12 hours at Appledore Island and on the R/V *Ronald H. Brown* (during the biomass burning event reported by Quinn *et al.* [2006]). During the time period between 12 July and

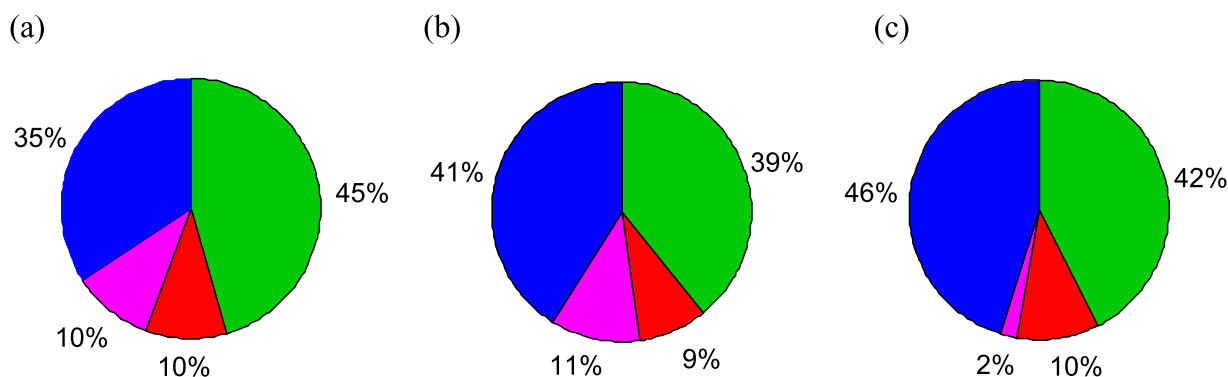


Figure 4. Project average OM composition on (a) the R/V *Ronald H. Brown*, (b) Chebogue Point, and (c) Appledore Island from 12 to 14 July. The color assignments for the organic functional group mass fractions is the same as in Figure 2.

noon on 13 July, Appledore Island was subject to northerly wind. The R/V *Ronald H. Brown* measured along the coast of New England and sampled air masses coming from the North, as indicated by retrorplume calculation. Figure 4 reports the average composition of the organic mass during the event occurred on 12 July, for R/V *Ronald H. Brown*, Chebogue Point and Appledore Island samples. At Chebogue Point, for the time period that goes from 12 to 13 July, 41% of organic mass is composed of saturated aliphatic C-C-H groups, 39% of carbonyl C=O groups, and 11% of organic hydroxyl C-OH groups. R/V *Ronald H. Brown* OM composition is characterized by a similar contribution of saturated aliphatic C-C-H groups (35%), organic hydroxyl C-OH groups (10%) and carbonyl C=O groups (45%). Appledore Island organic mass composition is similar to Chebogue Point, although a smaller contribution from organic hydroxyl C-OH groups was observed. The average functional group contribution to the total OM for 12–13 July differs from the project average reported in Figure 3 by its higher fraction of carbonyl C=O groups and lower fraction of organic hydroxyl C-OH groups.

[17] A second event observed at multiple platforms in the ICARTT region took place from 17 to 18 July. On 18 July, R/V *Ronald H. Brown* and Chebogue Point measurements showed similar concentrations in carbonyl C=O groups and aromatic C=C-H groups. The maximum concentration of aromatic C=C-H groups measured during this event was $1 \mu\text{g m}^{-3}$ on the R/V *Ronald H. Brown* (project average equal to $0.1 \mu\text{g m}^{-3}$) and $0.8 \mu\text{g m}^{-3}$ at Chebogue Point (project average equal to $0.05 \mu\text{g m}^{-3}$). From 16 to 19 July Chebogue Point was influenced by southerly wind, with retrorplume calculations indicating air masses coming from the Gulf of Maine. The organic composition was similar to the project average during the sample taken during 17–18 July, with the single sample being insufficient to show any statistically significant differences.

3.1. Saturated and Unsaturated Aliphatic Organic Functional Groups

[18] During most of the sampling period, the organic mass is dominated by the contribution of saturated aliphatic C-C-H and unsaturated aliphatic C=C-H groups. Both saturated and unsaturated organic compounds are released as primary emissions from both fossil fuel combustion and

biogenic emissions. Unsaturated aliphatic C=C-H groups can be produced during the combustion processes by dehydration of alcohols or cracking of alkanes during incomplete combustion [Oros and Simoneit, 2000; Simoneit, 2002]. Unsaturated aliphatic C=C-H groups are also produced from oxidation of aromatic units [Johnson et al., 2005; Seinfeld and Pandis, 1998]. Figure 5 shows unsaturated aliphatic C=C-H relative to saturated aliphatic C-C-H concentration for the four sampling platforms.

[19] Figure 5 shows four weak linear relationships in the ratios of unsaturated to saturated organic compounds, indicating similar ratios during the sampling period with small average differences for each of the four platforms. Twin Otter samples are characterized by unsaturated aliphatic C=C-H to saturated aliphatic C-C-H group ratios equal to 0.10 ($n = 25$); higher ratios were observed at the coastal platforms for Appledore Island (0.2, $n = 65$), Chebogue

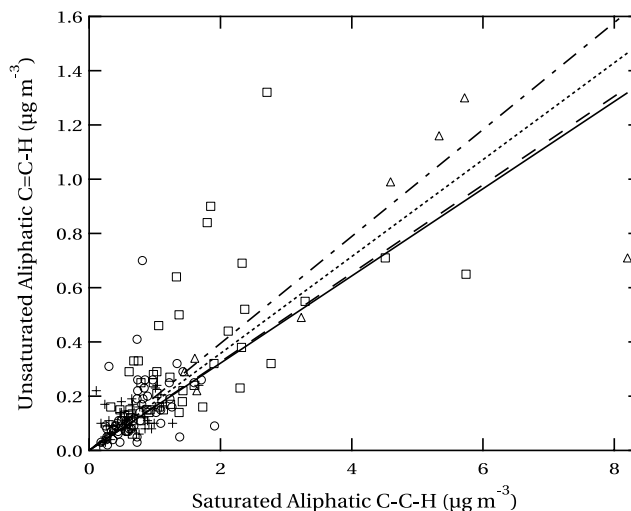


Figure 5. Ratios of saturated to unsaturated aliphatic C-H group concentration for Appledore Island (pluses), Chebogue Point (circles), R/V *Ronald H. Brown* (squares), and Twin Otter (triangles). Line fits for the different sampling sites are reported as solid line (Appledore Island), dotted line (Chebogue Point), dashed line (R/V *Ronald H. Brown*), and dot-dashed line (Twin Otter).

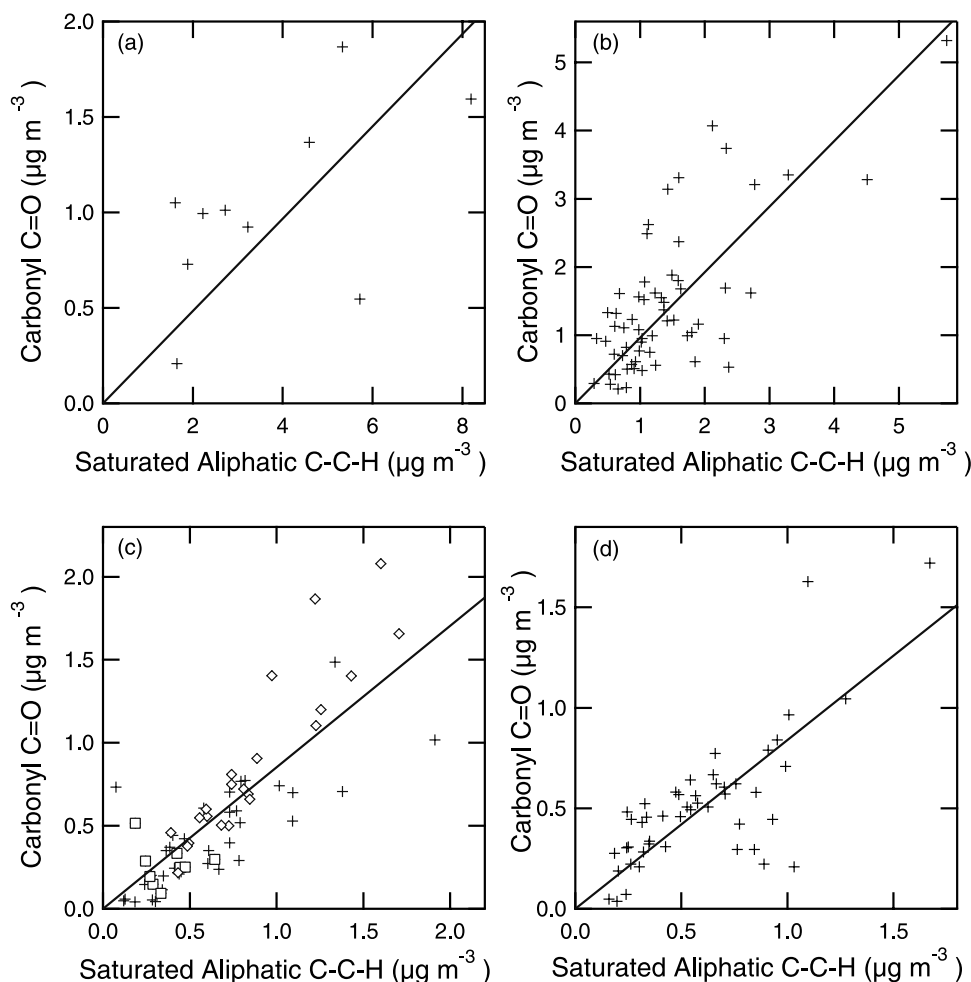


Figure 6. Ratios of carbonyl C=O to saturated aliphatic C-C-H group concentrations on (a) the Twin Otter, (b) the R/V *Ronald H. Brown*, (c) Chebogue Point, and (d) Appledore Island, indicated as pluses. For Chebogue Point, different symbols are used to indicate samples affected by Canada (diamond), U.S. (squares), and other (pluses) air masses.

Point (0.2, $n = 43$), and the R/V *Ronald H. Brown* (0.2, $n = 52$). These ratios are similar to the unsaturated to saturated C-H group concentration ratios of 0.2 to 0.5 which were measured by H-NMR of water soluble organic carbon (WSOC) from urban polluted areas [Fuzzi *et al.*, 2001; Decesari *et al.*, 2000]. The similarity of the average unsaturated to saturated aliphatic C-H group ratio observed at the three coastal sampling platforms suggests that those areas were often affected by air masses with similar sources. The higher average concentration of unsaturated compounds at the coastal platforms may indicate the larger contribution of biogenic sources or a lower contribution of saturated aliphatic C-C-H groups from unprocessed primary combustion emissions.

[20] Saturated aliphatic compounds dominate primary coal burning emissions [Oros and Simoneit, 2000]. For example, the bituminous coal combustion emission ratio of unsaturated to saturated aliphatic C-H is 0.02.

3.2. Oxygenated Organic Carbon

[21] Oxygenated functional groups (carbonyl C=O and organic hydroxyl C-OH) were observed on all platforms with concentrations that were often comparable to the

saturated aliphatic C-C-H group concentrations. Figure 6 shows carbonyl C=O group concentration relative to saturated aliphatic C-C-H concentration, for each platform. These molar ratios and correlation coefficients are reported in Table 2. The Twin Otter samples in Ohio were characterized by a lower molar ratio (0.1) compared to R/V *Ronald H. Brown* (0.5), Chebogue Point (0.5), and Appledore Island (0.4). The carbonyl C=O to saturated aliphatic C-C-H group molar ratios recorded on the R/V *Ronald H. Brown* and at the two coastal platforms are similar to the ratios measured by H-NMR on the WSOC of urban aerosol in the Po Valley, which ranged between 0.2 and 0.5 [Fuzzi *et al.*, 2001]. Overall the lower average carbonyl C=O group to saturated aliphatic C-C-H group ratio on the Twin Otter is consistent with the less aged emissions observed over Ohio [Sorooshian *et al.*, 2006] than those measured on the coastal platforms, as prior work indicated more carboxylic acids (containing more carbonyl groups) were typically associated with aged and secondary aerosol [Rogge *et al.*, 1993; Zhang *et al.*, 2005].

[22] The linear correlation between carbonyl C=O groups and saturated aliphatic C-C-H groups for each platform was significant at the 99% confidence level. The variability of

Table 2. Carbonyl C=O Group to Saturated Aliphatic C-C-H Group Molar and Average OM/OC Ratios for the Four Sampling Platforms and Air Mass Categories

Platform	C=O/C-H Molar Ratio ^a	OM/OC ^b
Twin Otter	0.1 (90)	1.4 (0.12) n = 25
R/V <i>Ronald H. Brown</i>	0.5 (99.9)	1.6 (0.14) n = 60
Appledore Island	0.4 (99.9)	1.5 (0.16) n = 79
Chebogue Point	0.5 (99.9) (Canada: 0.5 (99.9); United States: 0.3 (<75))	1.6 (0.14), n = 74 (Canada: 1.6 (0.11), n = 22; United States: 1.6 (0.18), n = 9)

^aThe significance of each linear regression was calculated by t-test and is reported in brackets.

^bStandard deviation is reported between brackets, where “n” indicates number of samples for each platform and category.

the ratio of carbonyl C=O groups to saturated aliphatic C-C-H groups indicates a range of oxygenated organic aerosol compositions in the air masses sampled at each platform during the course of the project. To study the variability in the degree of oxidation of aerosol samples collected at Chebogue Point, the air masses measured have been separated according to the retroplume calculations. “Canada” and “U.S.” categories correspond to air masses affected mainly by Canadian or U.S. emissions. Samples at Chebogue Point associated with air masses from Canada are characterized by a carbonyl C=O to saturated aliphatic C-C-H groups molar ratio equal to 0.5. These samples also generally show a higher ratio of carbonyl C=O to saturated aliphatic C-C-H groups compared to air masses from the United States which had a ratio of 0.3. Figure 7 reports the temporal variation of carbonyl C=O to saturated aliphatic C-C-H groups molar ratio for Chebogue Point. Thermal desorption aerosol GCMS-FID (TAG) data show that compounds associated with biogenic emissions are often present in high concentrations in the air masses with retroplumes dominated by emission sources in Canada. For a detailed description of TAG measurements refer to Williams *et al.* [2007]. The FTIR functional group composition indicates that these aerosol particles associated with aged biogenic emissions are enriched in carbonyl C=O groups relative to saturated aliphatic C-C-H groups.

3.3. OM/OC Ratios

[23] The ratio of organic mass to organic carbon (OM/OC) describes the overall organic composition of aerosol particles, providing a distinction between organic compounds dominated by hydrocarbons with ratios ranging from 1 to 1.2 and OM containing a significant fraction of oxygen, sulfur and nitrogen which have OM/OC from 1.3 to more than 2 [Russell, 2003]. Ambient measurements of organic mass are still scarce. In addition to the FTIR technique used here, OM can be estimated from AMS measurements of organic fragments [Allan *et al.*, 2004; de Gouw *et al.*, 2005] or determined by elemental analysis of organic fraction after extraction with water or organic solvents [El-Zanan *et al.*, 2005]. For the 4 different platforms and 2 different air mass categories, Table 2 lists the OM/OC ratios calculated from FTIR functional group composition. Each sampling platform shows low variability in OM/OC, suggesting that organic composition during the ICARTT experiment was fairly constant at each platform. OM/OC measured on the R/V *Ronald H. Brown* in the Gulf of Maine agrees with other reports of OM/OC for urban and polluted continental locations, including a study performed

in the Gulf of Maine in 2002 in which OM/OC was equal to 1.8 [de Gouw *et al.*, 2005]. OM/OC reported for IMPROVE platforms ranges between 1.6 and 2.6 [El-Zanan *et al.*, 2005]. The lower OM/OC ratio recorded during the Twin Otter campaign can be explained by the observation that fresh emissions contain lower concentrations of oxidized functional groups which reduces the associated OM/OC ratio [Turpin and Lim, 2001]. Table 2 shows that OM/OC at Chebogue Point does not differ significantly for the two air mass retroplume emission categories.

3.4. Organosulfur Compounds

[24] Organosulfur compounds are a minor component of organic aerosol mass. Organosulfur compounds were detected at all four of the sampling platforms studied for ICARTT 2004, with a higher frequency at Chebogue Point. The organosulfur C-O-S functional group absorbance can be associated with either sulfuric or sulfonic esters. These classes of compounds may be produced by addition of sulfuric or sulfonic acid to alkenes or by esterification of hydroxyl group promoted by the same acids [Romero and Oehme, 2005]. In the aqueous aerosol particles, carbonyl

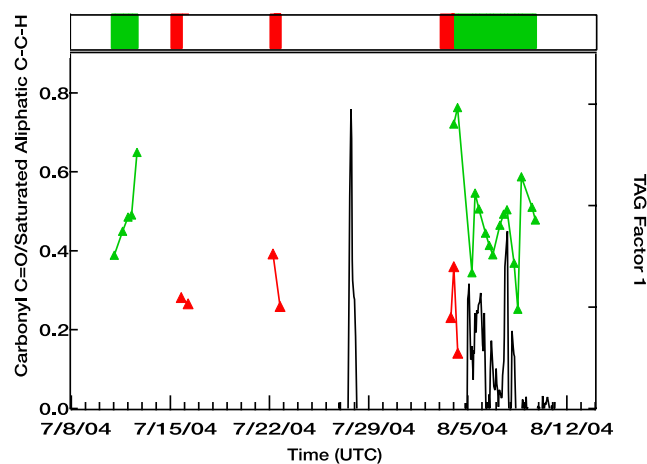


Figure 7. Time series of the ratio of carbonyl C=O groups to saturated aliphatic C-C-H group concentration ratio at Chebogue Point. The color of the symbols and the color bar at the top of the graph identify samples associated with air masses with emissions originating mostly from Canada (green) or the United States (red) (based on retroplume calculations). TAG factor 1 is a marker of biogenic emissions [Williams *et al.*, 2007] at Chebogue Point.

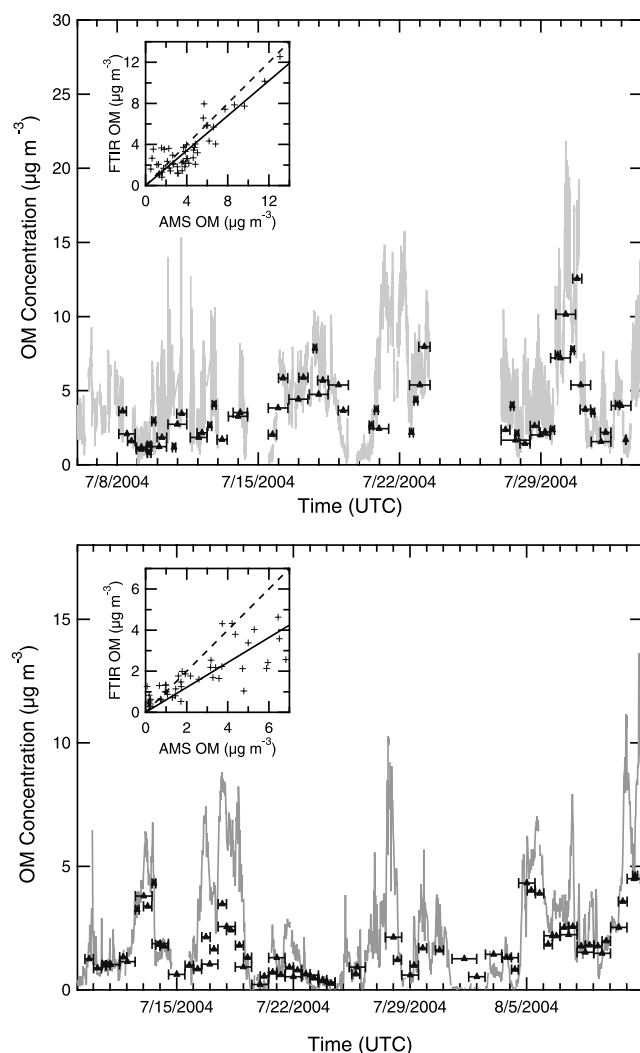


Figure 8. Comparison of AMS and FTIR OM on (a) the R/V *Ronald H. Brown* and (b) Chebogue Point. The time series of 5-min average AMS organic mass is shown as a grey line; FTIR organic mass is represented by black triangles. Horizontal error bars indicate the duration of the sampling time for each sample. Insets show scatterplots of AMS average OM versus FTIR OM for the times when sampling largely overlapped. The dashed line indicates the 1:1 ratio.

C=O functional groups may be converted into hydroxyl O-H group by several mechanisms including hydration and polymerization [Hastings *et al.*, 2005]. Reaction with sulfuric or sulfonic acid would produce sulfuric or sulfonic esters and would shift the partitioning of the original carbonyl compounds from the gas phase toward the particle phase. In this scenario, organosulfur compounds formation would explain the unusually high particle-to-gas phase distribution coefficient observed for some volatile carbonyl compounds [Hastings *et al.*, 2005]. Most of the samples in which organosulfur C-O-S groups were detected also had high organic mass loadings. Organosulfur C-O-S groups were detected only in samples that showed the simultaneous presence of sulfate and carbonyl species, with relative humidity higher than 80%.

3.5. Intercomparison of FTIR With AMS OM and TOA OC

[25] During the ICARTT experiment AMS measurements were collected on Chebogue Point and the R/V *Ronald H. Brown*. AMS measurements were used to calculate OM of aerosol samples by summing contributions from mass fragments containing carbon atoms [Allan *et al.*, 2004; Quinn *et al.*, 2006]. The Aerodyne AMS measurements used quadrupole systems as described by Jayne *et al.* [2000] and Jimenez *et al.* [2003]. The instrument is capable of measuring the submicron, nonrefractory component of the aerosols, using the data analysis techniques described by Allan *et al.* [2003, 2004]. For the Chebogue Point OM concentration measurements, a collection efficiency of 0.5 and relative ionization efficiency of 1.4 were used. More details of the instruments and their results are published by Williams *et al.* [2007]. Figure 8 shows a comparison of the time series of AMS and FTIR organic mass concentrations for Chebogue Point and R/V *Ronald H. Brown*. The insets on Figures 8a and 8b show the quantitative correlation between the AMS and FTIR OM measurements, for which the AMS organic mass concentrations were integrated for the filter sampling period. At Chebogue Point the average FTIR to AMS ratio is 0.6 ± 0.1 with a correlation coefficient equal to 0.80. The comparison of organic mass on the R/V *Ronald H. Brown* showed very similar trends in the time series in Figure 8a, and the inset shows that the ratio of the FTIR to AMS organic mass has a slope of 0.9 ± 0.1 and a high correlation coefficient ($r^2 = 0.87$).

[26] R/V *Ronald H. Brown* organic carbon (OC) was monitored by two Thermo-Optical Analysis (TOA) instruments with fast (45 to 105 min) and slow (4 to 8 hours)

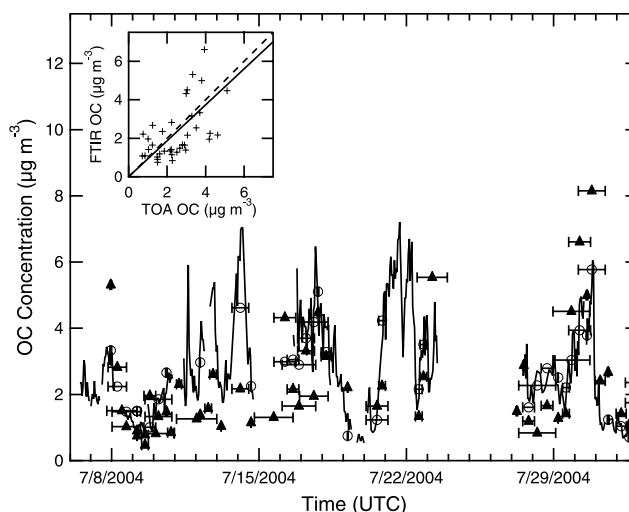


Figure 9. Comparison of TOA and FTIR OC for R/V *Ronald H. Brown* measurements. Time series of high time resolution online TOA OC is shown as a grey line, low time resolution filter TOA OC is shown as circles, and FTIR organic carbon is shown as black triangles. Horizontal error bars indicate the duration of the sampling time for each sample. Inset shows scatterplots of low time resolution TOA filter sample OC versus simultaneous FTIR OC for the times when sampling largely overlapped. The dashed line indicates the 1:1 ratio.

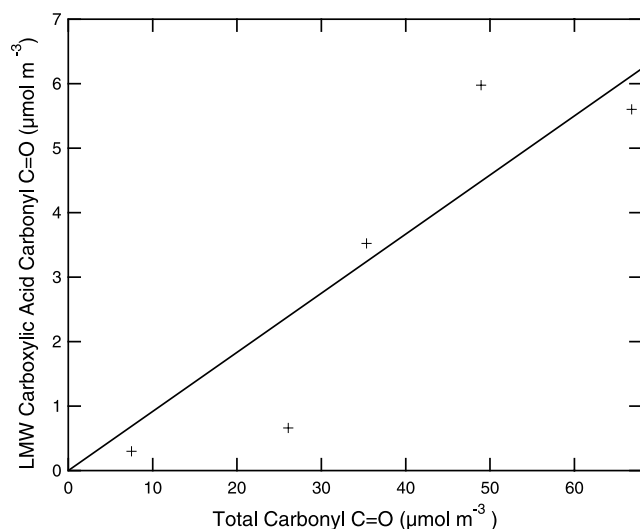


Figure 10. Carbonyl C=O group molar concentration of PILS LMW carboxylic acids plotted as a function of total FTIR carbonyl C=O group molar concentration.

sampling times [Schauer *et al.*, 2003; Quinn *et al.*, 2006]. The FTIR is lower than AMS OM on average at both sites, which may result from underprediction of heteroatoms in the FTIR algorithm [Russell, 2003] or overprediction of mass fragments by the AMS calibration [Quinn *et al.*, 2006] for some organic compositions. Figure 9 shows the comparison of TOA OC with FTIR OC for samples collected simultaneously, with a slope of 0.9 ± 0.1 and a correlation coefficient of 0.67. The higher scatter associated with the OC measurements may be a result of the uncertainty associated with inferring OC from measured functional groups [Russell, 2003].

3.6. LMW Carboxylic Acids and Carbonyl Groups on CIRPAS Twin Otter

[27] Low molecular weight (LMW) carboxylic acids were measured by PILS and IC during the Twin Otter flights over Ohio. The carboxylic acids measured were detected as oxalate, glyoxylate, glutarate, malonate, and pyruvate ions [Sorooshian *et al.*, 2006]. Oxalate concentration ranged between $0.01 \mu\text{g m}^{-3}$ and $0.3 \mu\text{g m}^{-3}$ during the sampling period overlapping to filter collection. Concentrations of glyoxylate, glutarate, malonate and pyruvate were generally one or two orders of magnitude lower than oxalate. The carbonyl C=O group fraction of the total measured LMW carboxylic acids was calculated for each FTIR sampling period and compared to the total carbonyl C=O group concentration determined by FTIR in Figure 10. Figure 10 reports carbonyl C=O group concentration from LMW carboxylic acid relative to total carbonyl C=O group concentration measured by FTIR. The number of points available for the comparison was limited but shows a linear correlation coefficient of 0.82 ($n = 5$). The slope of the fit shows that the LMW carboxylic acids represent 9% of the total carbonyl C=O groups detected by FTIR.

4. Conclusions

[28] Analysis by FTIR spectroscopy of aerosol particle samples collected at four different locations in eastern North

America show high concentrations of saturated aliphatic C-C-H groups and carbonyl C=O groups. The functional group composition shows significant differences across the ICARTT region: The Twin Otter sampled near large sources of primary organic emissions (including several large regional power plants) and measured lower unsaturated to saturated aliphatic C-C-H groups and lower OM/OC ratios compared to the coastal platforms (Chebogue Point, Apple-dore Island, and the R/V *Ronald H. Brown*). The average OM/OC ranged between 1.4 (for Twin Otter in Ohio and Chebogue Point) and 1.6 (for R/V *Ronald H. Brown* and Chebogue Point). Organic particles collected during the Twin Otter flights over Ohio show a lower carbonyl C=O group concentration relative to saturated aliphatic C-C-H group concentration than samples collected at the coastal locations, suggesting that fresh emissions are predominant in those samples.

[29] Some of the variability within the samples at each platform can be attributed to changes in air masses, with those air masses associated with similar regional sources also having comparable functional group composition. Retroplume analysis for Chebogue Point samples suggested that air masses that reached this location from Canada and showed TAG factors that were indicative of biogenic emissions, were characterized by higher carbonyl C=O group concentration relative to saturated aliphatic C-C-H groups, compared to those air masses dominated by U.S. sources.

[30] Intercomparison of independent techniques for measuring the total OM and OC at two of the sampling locations (i.e., Chebogue Point and R/V *Ronald H. Brown*) showed that the two techniques generally track each other with time (with slopes of 0.6 and 0.9, respectively) but the linear correlations show a high variability in the data, as is typical for intercomparisons of organic measurements [Turpin and Lim, 2001]. Comparison of carbonyl C=O group concentration with LMW carboxylic acid concentration shows that LMW carboxylic acids represented approximately 9% of the total observed carbonyl C=O groups for samples collected near plumes associated with coal power plants.

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